

DONOR SOLVENT REACTIONS WITH COAL IN A BATCH-RECYCLE SYSTEM

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INTRODUCTION

Numerous reports concerning kinetics of coal dissolution with hydrogen donor solvent are available. However, little knowledge about the primary products and the reactions which take place in experiments with short residence times have been reported until recently.

This study involved the dissolution of coal in hydrogen donor solvent (tetralin) in a rapid heat and rapid quench batch recycle system (Figure 1). The residence time of the coal-solvent slurry was in the range of a few seconds per pass in the slurry dissolver. The differential reactor system of batch recycle applied here had two main advantages compared with conventional autoclaves. 1) The rapid initial rate was expanded in the time scale of differential conversions; consequently, the initial conditioning period was minimized. In addition, continuous monitoring of data in a single run gave more definitive and smoother results which could probably not have been achieved by batch experiments. 2) A quench system was used which allowed only a few seconds of thermal exposure of the slurry (at the reaction temperature) per pass. This apparently reduced the reorganization and polymerization reactions of the primary reaction products and permitted the analysis of these primary fragmentation products from the dissolution process.

EXPERIMENTAL

A weighed amount of coal particles vehicle with small amounts of tetralin was vacuum fed into the slurry mixer. When addition of coal to the system was completed, hydrogen was used to purge and pressurize the system. Pumping of the coal-solvent slurry was carried out at room temperature for about 10 - 30 minutes while the slurry mixer was stirred at 1200 rpm to achieve complete suspension of the slurry throughout the system. The dissolver was heated to the reaction temperature to start the experiment. Less than three minutes was required to heat the slurry to 400°C in the dissolver. Flow velocity was 7.7 ft/sec when it was measured at the inlet to the preheater. Based on the conditions of 400°C and 1500 psig H₂, about six seconds of residence time of the slurry in the isothermal dissolver was achieved per pass. Slurry samples were taken at the mixer in sizes to minimize system disturbance. Slurry samples taken were weighed and centrifuged at 21,000 rpm for 40 minutes to separate solid residue and liquids. Liquid portions of the samples are subjected to gas chromatographic analysis to determine hydrogen transfer. Other methods of analysis were applied to the extracts from the reaction such as molecular weight and proton NMR.

Sequential washing of residual solids with fresh tetralin, benzene and pyridine was carried out to determine conversion data. Analysis of the ash content in the solid residues was used to determine the exact conversion figures. Gaseous products were collected in a liquid nitrogen double condenser in series at 77°K to trap the vapor products passing out through the gas vent. The rate of gas flow was kept to a minimum (approximately an average rate of 8 cc/sec at S.T.P.).

The following conditions were used for the system:

Temperature	
slurry dissolver	400°C ± 5°C
quench outlet	50-70°C

Note: Too low a temperature at the quench outlet was avoided to prevent wall deposition of products which could occur even at high turbulence (7.7 ft sec).

slurry mixer temperature	100°C ± 2°C
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Note: Low temperatures were avoided here for the same reason as above.

H ₂ preheater inlet	1650 psig
dissolver	1500 psig
slurry mixer	1350 psig

Coal : solvent ratio = 1 : 9

Coal = Bituminous coal, Hiawatha, Utah
(V.M. = 48.1%, F.C. = 43.3%, ash = 6.4%, S = 0.7%)

particle size: 270/400 mesh, sp gr < 1.35

Figure 2 shows overall conversions data (pyridine soluble + gas, benzene soluble + gas and total gas) as a function of the residence time of the reaction. One set of numbers on the time scale (lower numbers) shows actual accumulated run time which is a time scale based on differential reaction. The upper numbers on the time scale represent the true residence time calculated as if reaction were carried out integrally. When coal particles are homogeneously suspended throughout the system, the relationship between these two time scale holds that,

$$t_i = \frac{W}{w} t_d$$

where t_i = residence time in integral conversion

t_d = residence time in differential conversion

w = mass hold up in dissolver

W = mass hold up in the remainder of the reactor system

Figure 3 shows net naphthalene and other tetralin derived compounds vs. percent conversion. Table 1 shows the gas composition from gas chromatographic analysis. Table 2 shows molecular weights of the products measured by vapor pressure osmometry.

As shown in Table 2 the average molecular weights of both the cyclohexane soluble portion and the tetralin soluble and cyclohexane insoluble portions gradually decreased as conversion proceeded.

DISCUSSION OF RESULTS

Figure 2 represents conversion-time data in real time and differential time. Figure 3 shows the same data in terms of naphthalene formation vs. conversion. Naphthalene formation was used here to indicate hydrogen transfer. From the data in both figures, two separate reaction regimes may be visualized. The kinetics are initially very rapid with minimal H_2 transfer. After about 1.5 minutes the conversion rate decreases and the transfer of hydrogen increases.

During the initial stages of the reaction, gas formation appears to predominate as shown by the gas production in Figure 2 and low H_2 transfer in Figure 3. The rate of gas production rapidly decreased after about 1 minute as shown by the nearly horizontal part of the curve in Figure 2.

Formation of gaseous products appeared to be concentrated in the first stage of the reaction. As can be seen in Figure 3 a negligible amount of hydrogen appears to have been transferred in the initial stages of the reaction. After the inflection point the following regime of reaction (after about 27% benzene sol. + gas) consisted of a slower overall reaction but one involving a rapid hydrogen transfer (up to around 60% of the benzene soluble fraction). Again there appeared to be a decrease in the rate of hydrogen transfer after about seven minutes of actual reaction time. These phenomena are strikingly similar to what Neavel (1) found except that inflections of the conversion curves were not observed in Neavel's experiments. This may point out one advantage of using the differential reaction system employed in our experiments. The fact that tetralin is consumed less than 20 parts per 100 parts of coal for benzene soluble conversion levels of around 80% shows considerable discrepancy from many previous results. (For example, some others have shown up to 40 parts of tetralin converted per 100 parts of coal.) Although our results cannot be directly compared for example to Neavel due to different experimental conditions such as a different tetralin:coal ratio (9:1 compared to 2:1) and a hydrogen atmosphere in our experiments, some of the same trends were observed.

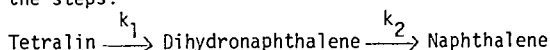
The initial regime of the dissolution reaction appeared to be controlled by thermal disintegration of the coal with evolution of gases. The lack of tetralin penetration into the micro (internal) pore structure of the coal (which is known to comprise about 80% of the total pores of the coal) seems to make the solvent-coal reaction less important during the initial stages. Also coal is known to be bimodal with sizes of the internal pores distributed around 5Å to 8Å which would make it difficult for tetralin molecules

(diameter about 10\AA) to enter these pores and make contact with internal reaction sites. Therefore, mere wetting of the external surface of coal may have taken place until opening of the micropores occurred by escaping trapped gases. An excess amount of solvent was supplied for the reaction (9:1 ratio of solvent to coal) since previous experiments by our laboratory and others showed that below approximately a 6:1 ratio of tetralin:coal the tetralin became the limiting reactant (2). Following the initial period of rapid donation of hydrogen from tetralin additional reaction paths may have been followed by introduction of tetralin into fresh reaction sites without restriction of diffusion into or out of the pores in the coal particles. The last stage of hydrogen donation appears to be controlled by diffusion either of fresh tetralin into the coal particles or products out of the particles. Even though the conversion rate is approximately constant (Figure 2) the hydrogen transfer rate after the initial rapid reaction is much less than the conversion rate as shown in Figure 3.

The data after about 10 minutes of actual reaction time for pyridine soluble and benzene soluble conversion were approximately the same. This is somewhat surprising since the initial reactions gave much higher benzene soluble yields. With the reaction system used the coal solvent mixture reached high temperatures followed by a quench which lowered the temperature to near ambient except during the time when the coal solvent mixture was in the reactor or heater. This gives some indication that perhaps this method of coal solvent interaction could improve product quality substantially.

The analysis of the gases which were released during the dissolution process which showed that methane formation was very small compared with that for other gases. This may or may not have implications as far as the linkages in the coal structure is concerned. As the carbon number of the molecules in the gas phase which appeared as products increased it is apparent from Table 1 that the fraction of the gases of a particular molecular weight which are normal straight chain hydrocarbon compounds decreased. This increasing ratio of unsaturates as the molecules became longer may be attributable to the longer lifetime of some free radicals which survive until the quench conditions change the temperature of the product mixture. As can be seen in Table 1 a substantial amount of isomers were formed for C4 compounds.

Substantial amounts of dihydronaphthalene were formed during the dissolution process. The formation of this dihydronaphthalene appears either to have been related to mild hydrogen transfer conditions or to have been an intermediate in the dehydrogenation of tetralin (or naphthalene formation). The majority of the dihydronaphthalenes were formed in a very short time in the initial stages of the reaction. The amount of these dihydronaphthalenes gradually decreased as conversion proceeded after giving a maximum at the first data point taken for the reaction at 400° (at about six seconds) as shown in Figure 3. In this tetralin excessive environment, dihydronaphthalene might follow the trends shown if it were an intermediate in a reaction path leading to naphthalene from tetralin. Such a consecutive reaction scheme would include the steps:



where the particular shape of the curves for dihydronaphthalene and naphthalene concentrations would depend on the relative values of k_1 and k_2 (assuming the reactions to be simple first order). The species resulting from the formation of dihydronaphthalene turned out to be over 99% of 1, 2-dihydronaphthalene. Hexa-, octa-, and decahydronaphthalene concentrations follow the same trends as given by Neavel (1) although he showed smaller quantities formed. This is probably to be expected since his conditions and coal/solvent ratio were different. The formation of cis-decalin always prevailed over trans-decalin. The results concerning dihydronaphthalenes and decalins needs mechanistic explanation and further experimental work will probably have to be done to explain the results obtained. Especially important is precise analyses of all of the chemical species present as a function of reaction time (or extent of reaction).

REFERENCE

1. R. C. Neavel, "Liquefaction of Coal in Hydrogen Donor and Non-Donor Vehicles", FUEL, Vol. 55, July, 1976.
2. W. H. Wiser and G. R. Hill, A Kinetic Study of the Thermal Dissolution of High-Volatile Bituminous Coal, Symposium of Science and Technology of Coal, Ottawa, Canada, 1967, p. 162-167.

Table 1. Gaseous Compounds
(collected in liquid nitrogen at 77°K (-196°C))
From reaction of tetralin with Hiawatha Coal at 400°C
(Tetralin:coal = 9:1; weight basis)

Compound	%	% Composition in each Homologs	Composition sat/unsat.	% Composition of Homologs
C ₁	.3	100	100/0	.3
C ₂	32.6	82	82/18	39.7
C ₂ =	7.1	18		
C ₃	25.0	69	69/31	36.2
C ₃ =	11.2	31		
iC ₄	1.7	14*	60/40	12.1
C ₄	5.6	46		
1&iC ₄ =	.9	7*		
t,C2C ₄ =	3.9	33		
n,iC ₅	3.5	56**	56/44	6.2
allC ₅ =	2.8	44		
allC ₆	5.1			5.1
allC ₇	.6			.6
allC ₈	.3			.3

* substantial amount of isomers

**mostly normal with small amount isomer on shoulder

Notes:

1. % Composition based on gaseous products up to C₈ vapors collected.
2. Gas chromatographic analysis with the following conditions:
20 ft. activated alumina (F-1)
program temperatures from 60°C to 280°C (8°C/min.)
He carrier gas flow rate = 30 ml/min.

Table 2. Molecular Weight of Extraction Products
from Coal Extraction with Tetralin at 400°C

Conversion (benzene soluble)	Cyclohexane soluble	Cyclohexane insoluble Tetralin soluble
11.5	669	1506
27.7	539	15070
31.4	794	1368
42.5	504	1288
58.6	430	1126
77.5	436	1203

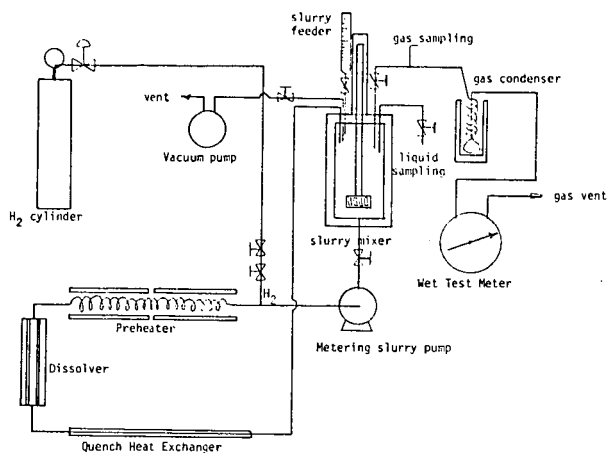
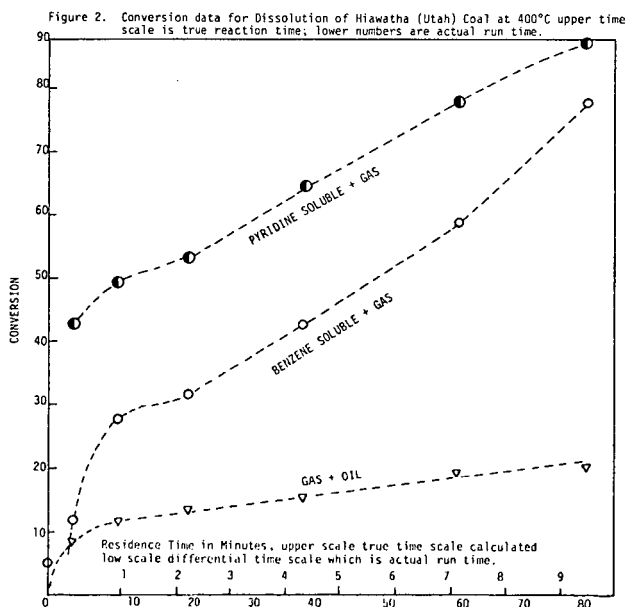


Figure 1. Batch recycle system for dissolution of coal in a hydrogen donor solvent.



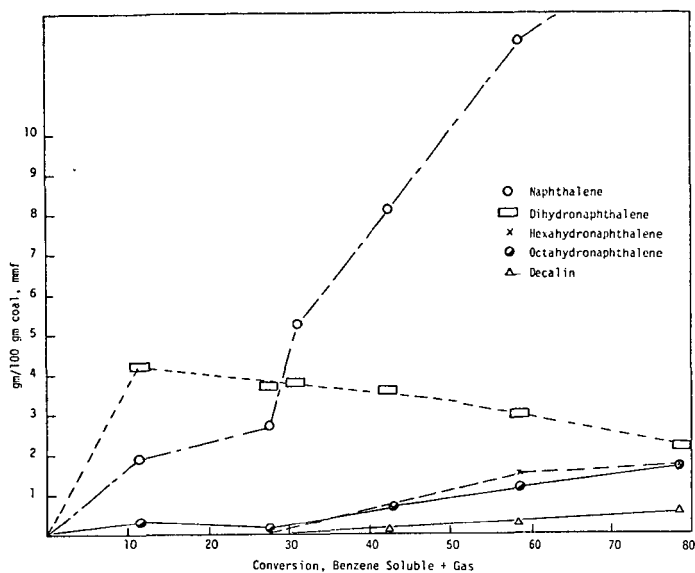


Figure 3. Hydrogen transfer as measured by tetralin derivatives from reactions with coal at 400°C (Hiawatha Coal)

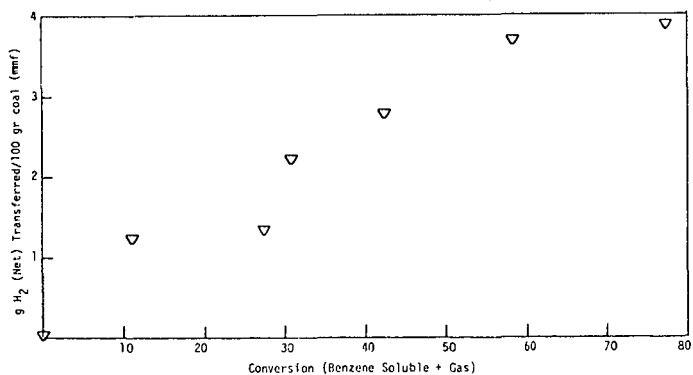


Figure 4. Net Hydrogen Transfer from Tetralin at 400°C in Reactions with Hiawatha Coal.